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Eugenya V. Makoveeva, Dmitri V. Alexandrov, and Alexander A. Ivanov

A Complete Analytical Solution to the Integro-Differential Model for Nucleation and Evolution of Crystals in a Metastable System

Eugenya V. Makoveeva[a)], Dmitri V. Alexandrov[b)] and Alexander A. Ivanov[c)]

Department of Theoretical and Mathematical Physics, Laboratory of Multi-Scale Mathematical Modeling, Ural Federal University, Ekaterinburg 620000, Russian Federation

[a)]Corresponding author: eugenya1m@gmail.com
[b)]dmitri.alexandrovr@urfu.ru
[c)]alexandr.a.ivanov@bk.ru

Abstract. A nonlinear system of time-dependent integro-differential equations that describes the processes of phase transformations in metastable melts and solutions is investigated. Using the saddle-point method for calculating the Laplace-type integral, a complete analytical solution was constructed, which determines the dynamic dependencies of the crystal size distribution function and the supercooling (supersaturation) of the system. The maximum size of the growing crystals, the average number of crystals and their average size as functions of time are found. It is shown that to correctly describe the evolution of a metastable system, it is necessary to take into account both the fundamental contribution of the saddle-point method and the following four contributions of the asymptotic expansion. The theory under consideration is in good agreement with experimental data.

INTRODUCTION

At the initial stages, the process of evolution of a metastable system can be considered, neglecting the influence of crystallites growing in it, both at each other and at the degree of supercooling or supersaturation. Over time, when the number of crystals in the system increases, they begin to have a significant impact on the degree of metastability, reducing it due to the release of the latent heat of the phase transition (in the case of supercooled melts) or absorption of the dissolved impurity (in the case of supersaturated solutions). In this case, the process of nucleation continues and a certain particle size distribution appears in the system, which is described using the distribution function. The mathematical model of the process at this stage, called the intermediate, is an integro-differential system consisting of the Fokker-Planck equation for the distribution function and the balance equation for the degree of metastability [1–5]. Such a model is closed using appropriate boundary and initial conditions, which strongly depend on the kinetic mechanisms of crystal growth (for example, the kinetic mechanisms of Meirs and Weber-Volmer-Frenkel-Zeldovich), as well as the expressions used for the dependencies of the crystal growth rates on the degree of metastability, and sometimes even on the radius of the crystals and time [6–8]. The complexity of the mathematical formulation of an integro-differential problem with moving phase transition boundaries indicates the absence of general methods for its theoretical analysis so that each individual model deserves special consideration and development of original approaches for its theoretical or numerical study. At the final stage of phase transformation, the mathematical formulation of the problem is further complicated by the need to take into account the processes of coalescence, coagulation, and fragmentation of particles [9–16].

The present study is devoted to an analytical description of the nonstationary process of nucleation and growth of particles at the intermediate stage of phase transformation in metastable melts and solutions. The paper takes into account a power-law empirical dependence for the growth rate of spherical nuclei, as well as the kinetics of their nucleation, according to the Meirs and Weber-Volmer-Frenkel-Zeldovich (WVFZ) mechanisms [17, 18].

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THE MODEL

The evolutionary behavior of the dimensionless degree of metastability $u(\tau)$ and the particle-radius distribution function $f(\tau, l)$ (here τ and l represent the dimensionless time and spatial variables) is characterized by the following balance and kinetic equations [19, 20]

$$\frac{du}{d\tau} = -b_1 u^m \int_0^\infty l^2 f(l,\tau) dl,\ \tau > 0, \tag{1}$$

$$\frac{\partial f}{\partial \tau} + u^m \frac{\partial f}{\partial l} = 0,\ \tau > 0,\ l > 0, \tag{2}$$

where b_1 is a positive parameter [19, 20]. Equations (1) and (2) should be supplemented by the boundary conditions of the form

$$u = 1,\ f = 0,\ \tau = 0; f = \frac{1}{u^m} \exp[p\phi(u)],\ l = 0, \tag{3}$$

where p is a positive constant and ϕ reads as

$$\phi(u) = \begin{cases} 1 - u^{-2}, \text{WVFZ (sm)}, \\ \ln^{-2}(1 + u_p^{-1}) - \ln^{-2}(1 + u/u_p), \text{WVFZ (ss)}, \\ \ln u, \text{ Meirs (sm and ss)}, \end{cases} \tag{4}$$

where symbols sm and ss designate the supercooled melts and supersaturated solutions, $u_p = C_p/\Delta C_0$, C_p and ΔC_0 are the concentration at saturation and supersaturation.

The dimensionless growth rate for spherical particles can be written out as [17, 18]

$$\frac{dl}{d\tau} = [u(\tau)]^m \tag{5}$$

where m is a positive constant.

A COMPLETE ANALYTICAL SOLUTION

Taking into account the boundary conditions (3) let us express the exact solution of equation (2) as

$$f(l,\tau) = \Sigma(y(\tau) - l)\eta(y(\tau) - l),\ \Sigma(u) = \frac{\exp[p\phi(u)]}{u^m},\ y(\tau) = \int_0^\tau u^m(\tau_1) d\tau_1, \tag{6}$$

where η is the Heaviside function. Integrating the rate of crystal growth (5), we have ($l = 0$ at $\tau = \mu$)

$$l = y(\tau) - y(\mu). \tag{7}$$

Equation (7) at $\mu = 0$ gives the maximal size $l_m(\tau)$ of spherical particles that originated at zero time, i.e. $l_m(\tau) = y(\tau)$. Now we use the new variable μ instead of l accordingly to the following substitution

$$y(\mu) = y(\tau) - l. \tag{8}$$

Let us emphasize that the limits $l = 0$ and $l = l_m(\tau)$ of integration transform to the limits $\mu = \tau$ and $\mu = 0$. Now equations (7) and (8) lead to

$$\frac{du}{d\tau} = -b_1 u^m \int_0^\tau q(\mu,\tau) \exp[p\phi(\mu)] d\mu, \tag{9}$$

Table 1. Coefficients of the analytical solution

	WVFZ (sm)	WVFZ (ss)	Meirs (ss and sm)
$\phi^{(\mathrm{IV})},\ \mu = 0$	$-4b_1$	$-4\kappa b_1$	$-2b_1$
$\phi^{(\mathrm{VIII})},\ \mu = 0$	$16b_1^2(7m + p)$	$16b_1^2\kappa(7m + \kappa p)$	$4b_1^2(14m + p)$
$H(0)$	$-\chi/4$	$-\kappa^{-1/4}\chi/4$	$-2^{1/4}\chi/4$

where

$$q(\mu, \tau) = [y(\tau) - y(\mu)]^2. \tag{10}$$

To use the Laplace method for the evaluation of integral in equation (9), we assume that $p \gg 1$. Expression (4) demonstrates that the derivative of ϕ with respect to μ is negative for both kinetic mechanisms under consideration. So, for example, in the case of supercooled melts, we arrive at

$$\frac{d\phi}{d\mu} = \begin{cases} 2u^{-3}\dfrac{du}{d\mu}, \text{ WVFZ} \\ u^{-1}\dfrac{du}{d\mu}, \text{ Meirs} \end{cases}. \tag{11}$$

Note that $du/d\mu < 0$ because the system metastability decreases with time and $u > 0$. Keeping this in mind, one can see that $\phi(\mu)$ attains a maximum value at $\mu = 0$. Now to use the saddle-point technique, we evaluate the first non-zero derivative of $\phi(\mu)$ at $\mu = 0$. Our results demonstrate that the first three derivatives vanish at $\mu = 0$ for both kinetics and only the fourth derivative is nonzero (for details, see Table 1), where

$$\chi = \left(\frac{6}{b_1}\right)^{1/4},\ \kappa = \frac{1}{(1 + u_p)\ln^3(1 + u_p^{-1})}.$$

So, the integral (9) can be evaluated as [21]

$$\int_0^\tau \exp[p\phi(\mu)]d\mu \approx \sum_{k=0}^{\infty} p^{-(k+1)/4} a_k(y), \tag{12}$$

$$a_k(y) = (-1)^{k+1}\frac{4^k}{k!}\Gamma\left(\frac{k+1}{4}\right)H^k(0)\frac{d^k}{d\mu^k}[q(\mu, \tau)H(\mu)]_{\mu=0}, \tag{13}$$

where Γ is the gamma function and

$$H(\mu) = \frac{[\phi(\mu)]^{3/4}}{\phi'(\mu)}. \tag{14}$$

To evaluate $H(\mu)$ and its derivatives at $\mu = 0$ we expand this function in series at $\mu = 0$ keeping in mind the nonzero derivatives $\phi(\mu)$ at $\mu = 0$ listed in Table 1. Substituting (14) into (13), we obtain $a_k(y)$ ($H'(0) = H''(0) = H'''(0) = 0$) in the form

$$a_0(y) = -\Gamma\left(\frac{1}{4}\right)H(0)y^2,\ a_1(y) = -8\Gamma\left(\frac{1}{2}\right)H^2(0)y,\ a_2(y) = -16\Gamma\left(\frac{3}{4}\right)H^3(0),\ a_3(y) = 0,$$

$$a_4(y) = -A_4y^2,\ A_4 = \frac{32}{3}\Gamma\left(\frac{5}{4}\right)H^4(0)H^{(\mathrm{IV})}(0),\ H^{(\mathrm{IV})}(0) = \frac{24^{1/4}\phi^{(\mathrm{VIII})}}{224(-\phi^{(\mathrm{IV})})^{5/4}},$$

where $H(0)$, $\phi^{(\mathrm{IV})}$, $\phi^{(\mathrm{VIII})}$ are presented in Table 1.

Now keeping in mind that

$$\frac{du}{d\tau} = \frac{du}{dy}\frac{dy}{d\tau} = u^m\frac{du}{dy}, \tag{15}$$

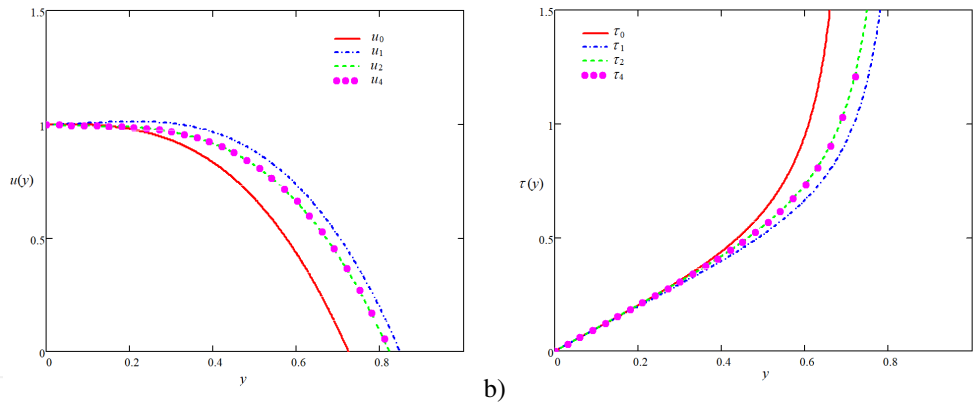

Figure 1. The dimensionless degree of metastability (a) and time (b) as functions of the modified time variable.

we have from expressions (9) and (12)

$$\frac{du}{dy} = -b_1 \sum_{k=0}^{\infty} p^{-(k+1)/4} a_k(y). \tag{16}$$

Integrating (16), we come to a parametric form of metastability expressed in terms of the modified time variable y

$$u(y) = 1 - b_1 \sum_{k=0}^{\infty} p^{-(k+1)/4} \int_0^y a_k(y_1) dy_1. \tag{17}$$

The $i-$th approximation of $u(y)$ is described by coefficients a_0, a_1, ..., a_k and takes the form

$$u(y) = u_i(y) = 1 - b_1 \sum_{k=0}^{i} p^{-(k+1)/4} \int_0^y a_k(y_1) dy_1. \tag{18}$$

The first five approximations have the form

$$u_0(y) = 1 + \Gamma\left(\frac{1}{4}\right) \frac{b_1 H(0) y^3}{3p^{1/4}},\ u_1(y) = u_0(y) + \Gamma\left(\frac{1}{2}\right) \frac{4b_1 H^2(0) y^2}{p^{1/2}}, \tag{19}$$

$$u_2(y) = u_3(y) = u_1(y) + \Gamma\left(\frac{3}{4}\right) \frac{16 b_1 H^3(0) y}{p^{3/4}},\ u_4(y) = u_2(y) + \frac{A_4 b_1 y^3}{3p^{5/4}}. \tag{20}$$

The dimensionless time and its $i-$th approximation can also be expressed as a parametric function of y from (15) as

$$\tau(y) = \int_0^y \frac{dy_1}{u^m(y_1)},\ \tau_i(y) = \int_0^y \frac{dy_1}{u_i^m(y_1)}. \tag{21}$$

Now combining (6) and (17), we get

$$f(y, l) = \frac{1}{u^m(y-l)} \exp\left[\frac{p(1-u^2(y-l))}{u^2(y-l)}\right] \eta(y-l). \tag{22}$$

Let us note that the radii of particles are bounded by the maximum size $l_m(\tau)$.

The total number of particles per unit volume and the mean radius of growing crystals are described as

$$N(y) = \frac{1}{l_0^3} \int_0^{l_m(y)} f(l, y) dl,\ \bar{L}(y) = l_0 \int_0^{l_m(y)} l F(l, y) dl \left(\int_0^{l_m(y)} f(l, y) dl \right)^{-1}. \tag{23}$$

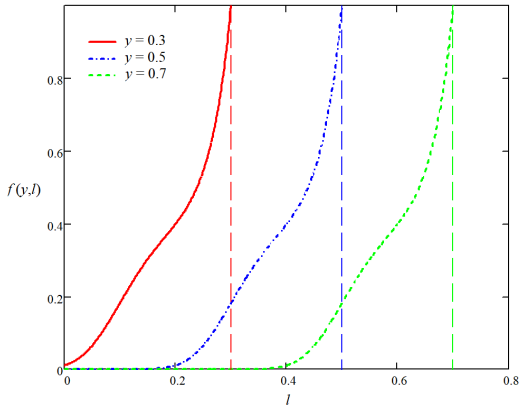

Figure 2. The dimensionless distribution function. The vertical lines show the maximal radius of the crystals.

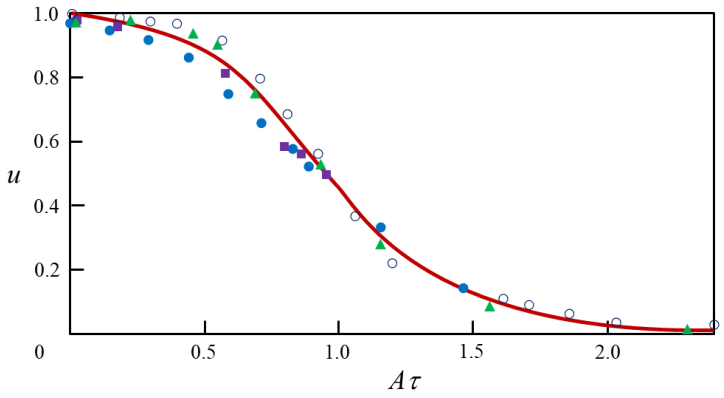

Figure 3. The dimensionless degree of metastability as a function of rescaled time: theory (solid line), experiment (filled symbols) with different initial supersaturations [22], and experiment (open circles) [23].

CONCLUDING REMARKS

Figures 1 and 2 show the obtained analytical solutions in a parametric form (where y plays the role of the parameter). The degree of system metastability decreases with increasing the modified time y and, as a consequence, with increasing the dimensionless time τ. The size-distribution function grows up to the maximal crystal radius existing in a metastable liquid. Figure 3 illustrates the present analytical solution versus experimental data for the degree of system metastability. The theory under consideration well agrees with experiments.

Let us especially emphasize in conclusion that the present theory should be generalized to take into account the growth of dendritic crystals in a metastable liquid in the spirit of recently developed theories [24–28].

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References

[1] Y. A. Buyevich and V. V. Mansurov, J. Cryst. Growth. **104**, 861–867 (1990).
[2] Y. A. Buyevich, V. V. Mansurov, and I. A. Natalukha, Chem. Eng. Sci. **46**, 2573–2578 (1991).

[3] D. V. Alexandrov, Phys. Lett. A **378**, 1501–1504 (2014).
[4] D. V. Alexandrov, J. Phys. A: Math. Theor. **47**, p. 125102 (2014).
[5] E. V. Makoveeva and D. V. Alexandrov, Phil. Trans. R. Soc. A **377**, p. 20180210 (2019).
[6] D. V. Alexandrov and I. V. Alexandrova, Phil. Trans. R. Soc. A **377**, p. 20180209 (2019).
[7] D. V. Alexandrov, I. G. Nizovtseva, and I. V. Alexandrova, Int. J. Heat Mass Transfer **128**, 46–53 (2019).
[8] D. V. Alexandrov, J. Phys. A: Math. Theor. **51**, p. 075102 (2018).
[9] E. M. Lifshitz and L. P. Pitaevskii, *Physical Kinetics* (Pergamon, Oxford, 1981).
[10] I. M. Lifshitz and V. V. Slyozov, J. Phys. Chem. Solids **19**, 35–50 (1961).
[11] J. R. Hunt, J. Fluid Mech. **122**, 169–185 (1982).
[12] Y. Enomoto and A. Okada, J. Phys.: Condens. Matter **2**, 4531–4535 (1990).
[13] A. V. Alyab'eva, Y. A. Buyevich, and V. V. Mansurov, J. Phys. II France **4**, 951–957 (1994).
[14] D. V. Alexandrov, J. Phys. A: Math. Theor. **48**, p. 035103 (2015).
[15] D. V. Alexandrov, J. Phys. A: Math. Theor. **48**, p. 245101 (2015).
[16] D. V. Alexandrov, Phil. Mag. Lett. **96**, 355–360 (2016).
[17] E. B. Treivus, *Kinetics of Growth and Dissolution of Crystals* (Leningrad State Univ., Leningrad, 1979).
[18] R. F. Strickland-Constable, *Kinetics and Mechanisms of Crystallization* (Academic Press, London, 1968).
[19] D. V. Alexandrov and A. P. Malygin, J. Phys. A: Math. Theor. **46**, p. 455101 (2013).
[20] D. V. Alexandrov, Phil. Mag. Lett. **94**, 786–793 (2014).
[21] M. V. Fedoruk, *Saddle-Point Method* (Nauka, Moscow, 1977).
[22] J. W. Mullin and C. J. Leci, AIChE J. Symp. Ser. **68**, 8–20 (1972).
[23] J. Carside, C. Gaska, and J. W. Mullin, J. Cryst. Growth **13/14**, 510–516 (1970).
[24] D. V. Alexandrov, P. K. Galenko, and L. V. Toropova, Phil. Trans. R. Soc. A **376**, p. 20170215 (2018).
[25] P. K. Galenko, D. V. Alexandrov, and E. A. Titova, Phil. Trans. R. Soc. A **376**, p. 20170218 (2018).
[26] D. V. Alexandrov, A. A. Ivanov, and I. V. Alexandrova, Phil. Trans. R. Soc. A **376**, p. 20170217 (2018).
[27] E. V. Makoveeva and D. V. Alexandrov, Phil. Trans. R. Soc. A **376**, p. 20170327 (2018).
[28] D. V. Alexandrov and I. G. Nizovtseva, Phil. Trans. R. Soc. A **377**, p. 20180214 (2019).